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DIAMOND CHEMICAL VAPOR DEPOSITION APPARATUS

Japan Kokai Takkyo Koho JP 62,216,998 [87,216,998]
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16. Abstract

The title app. is characterized by a cooling means provided for the substrate which is placed in an irradn. range of a thermionic emitter. The cooling means may be a supply of water or liq. N_2 or He into hollow(s) in or pipes on the substrate holder, or movement of the substrate holder outside the irradn. range. A diamond film was grown at 3 μm/h and 980° using a H_2O-cooled Mo substrate holder while a diamond was grown at 0.3 μm/h and 1400° without cooling.

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(54) Title of Invention: Diamond Chemical Vapor Deposition Apparatus

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Specification

/597

1. **Title of the Invention: Diamond Chemical Vapor Deposition Apparatus**

2. **Claims: It Is Claimed:**

(1). Diamond chemical vapor deposition apparatus which consists of a reactor with (a) gas pipe(s), a thermionic emitter which is set in the reactor, and a substrate holder which is installed in an irradiation range of the thermionic emitter, the novelty of the apparatus being a substrate holder cooling structure.

(2). Diamond chemical vapor deposition apparatus in Claim (1), the novelty of which lies in that the cooling struture is created by introducing water, liquid nitrogen or liquid helium into hollow(s) of the substrate holder which has been made hollow.

(3). Diamond chemical vapor deposition apparatus in Claim (1), the novelty of which lies in that the cooling structure is created by introducing water, liquid nitrogen or liquid helium into the pipe(s) which have been provided on the surface of the substrate holder.

(4). Diamond chemical vapor deposition apparatus in Claim (1), the novelty of which lies in the cooling structure, in which the substrate holder can be moved outside an irradiation range of the thermionic emitter.

3. **Detailed Description of the Invention**

Applicable Fields in Industries

This invention pertains to diamond chemical vapor deposition apparatus, possessing a thermionic emitter to produce diamond. The diamond can be used in various industries. Examples of uses are as follows: industrial tools such as cutting tool , wear-resistant tools, and abrasives; nuclear

*Nos. in margin indicate pagination of foreign text.

reactor parts such as reactor wall; electronic parts such as heat sink and speaker diaphragms; and precision machinery such as cameras and watches.

Description of Prior Arts

There are several kinds of apparatus to synthesize diamond from vapor phase. They are apparatus using sputtering, apparatus using ion-plating method, apparatus which combines vacuum evaporation and ion injection, apparatus using plasma-chemical vacuum evaporation by micro waves or high frequency waves, and apparatus using thermionic emitters.

Out of these diamond chemical vapor deposition apparatus, the /598
apparatus using thermionic emitters has advantages that gas control of the reactor can be easily done, resulting in a continuous production of diamond, and that diamond thus obtained is more likely to be a better, uniform granular diamond and film-like diamond.

Tokkai Sho 58-91100 Gazette and Tokkai Sho 60-221395 Gazette disclose Specifications which pertain to a method to synthesize diamond by chemical vapor deposition apparatus using a thermionic emitter.

Objects

Tokkai Sho58-91100 Gazette contains a method to synthesize diamond by chemical vapor deposition apparatus using a thermionic emitter, the novelty of which lies in that the surface of the substrate is heated to 500°C-1300°C. However, this method has a disadvantage that diamond deposition speed is extremely low. Tokkai Sho60-221395 has solved the above problem. Tokkai Sho60-221395 employs diamond chemical vapor deposition apparatus which is equipped with a thermionic emitter, the novelty of this method being that the thermionic emitter becomes negative and the substrate becomes positive by the application of direct current voltage. However, both Tokkai Sho58-91100 and Tokkai Sho60-221395 methods

require to heat tne thermionic emitter as hot as possible, resulting in a problem that the substrate becomes heated by the radiation of the heated thermionic emitter. Also, when the substrate is overheated the substrate is distorted and damaged by heat. In addition, diamond deposition rate becomes slow.

This invention has solved the problems described above. This invention presents a diamond chemical vapor deposition apparatus which is equipped with a substrate holder cooling structure, which cools the substrate heated by the radiation of a thermionic emitter.

Means to Achieve the Objects

When the authors of this invention were conducting an experiment of diamond deposition using chemical vapor deposition apparatus equipped with a thermionic emitter, with the object of the experiment being diamond deposition on the substrate surface, the inventors found that the hotter a thermionic emitter became, the more diamond deposition occurred due to an increased amount of gas but that the radiation heat from the thermionic emitter became so high that the substrate damage became great. The authors also found that although it was preferable to place a substrate as close to the thermionic emitter as possible in order to increase diamond deposition but that the substrate was affected greatly by the thermionic emitter radiation, resulting in a damage to the substrate and, ultimately, a difficulty of diamond deposition on the substrate surface. After more research, this invention was perfected when diamond chemical vapor deposition apparatus equipped with a cooling structure for the substrate was invented. This c ling system prevents a thermionic emittance radiation from affecting the substrate, resulting in an easier diamond deposition on the substrate surface.

In other words, the diamond chemical vapor deposition apparatus of this invention consists of a reactor with (a) gas pipe(s), a thermionic emitter installed in the reactor and a substrate holder placed in the radiation range of the thermionic emitter and is characterized by the substrate holder cooling system.

A reactor for the diamond chemical vapor deposition apparatus of this invention may take any form as long as it is possible to regulate vacuum or gaseous atmosphere in the reactor. A thermionic emitter to be placed in this reactor is used either as a heat filament or heat source. Examples for a thermionic emitter are as follows: tungsten, molybdenum, tantalum; the above elements, the surface of which is covered with tungsten carbide, titanium carbide, and titanium nitride; tungsten carbide. A substrate holder, which is to hold a substrate, which is for deposition of diamond and/or diamond-like carbon. There are no restrictions regarding the material of the substrate holder as long as there will be no deformation due to the radiant heat. Examples of suitable materials are as follows: ferroalloy such as stainless steel and carbon steel; nickel alloy such as Hastelloy and Inconel; cobalt alloy such as Stellite.

A substrate holder cooling structure can take any form as long as the substrate, which is held by the holder, can be cooled. For example, make the inside of the substrate holder hollow. Then introduce water, liquid nitrogen or liquid helium into the hollow of the substrate holder and circulate the liquid from outside the reactor. This cooling system cools the substrate and ease the effect of the thermionic emitter irradiation, resulting in a promotion of diamond deposition and/or diamond-like carbon. If a substrate can not be installed directly on the holder surface, a cooling structure can be (a) pipe(s) which is(are) installed to

the substrate holder surface, with water, liquid nitrogen or liquid helium being introduced into the pipe(s) to cool the substrate. Also, in order to minimize problems arising from substrate shapes or mass production of diamond, a substrate holder can be moved to outside an irradiation range of a thermionic emitter. For example, install several substrates on a substrate holder which can be rotated, and move the substrate to outside the irradiation range of the thermionic emitter so that the substrate, which is held by the holder, can be cooled. Or further cooling of a substrate, which is held by a substrate holder, can be done outside an irradiation range, by introducing water, liquid nitrogen or liquid helium into (a) pipe(s), as required.

In other words, diamond chemical vapor deposition apparatus of this invention is equipped with a structure to cool a substrate which is installed for diamond and/or diamond-like carbon deposition. With this cooling structure, the apparatus of this invention promotes deposition of diamond and/or diamond like carbon greatly. Also, the apparatus of this invention greatly lessens heat damage of a substrate by a thermionic emitter irradiation and promotes deposition of diamond and/or diamond-like carbon of better quality.

Examples

Example 1

Diamond was synthesized using chemical vapor deposition apparatus of this invention shown in Figure 1. A thermionic emitter of tungsten(3), and molybdenum substrate(5) on a substrate holder(4) were placed in a reactor with a gas pipe(2), with the substrate holder(4) being placed within an irradiation range of the thermionic emitter(3). Cooling capability was provided by the water circulated by the circulator(6) inside

of the substrate holder(4), which had been made hollow.

First, the inside of the reactor was evacuated through an exhaust pipe(7). Then, a gas of 99 volume percent helium and 1 volume percent methane was introduced into the reactor through the gas pipe(2). Diamond deposition was conducted with the thermionic emitter(3) temperature at 2000°C, the distance between the substrate(5) and the thermionic emitter(3) 3mm, while the substrate(5) was being cooled by the water circulated by the circulator(6). The result after one hour was film diamond of high crystallinity on the substrate surface. The thickness of the diamond was 3μm. The temperature of the substrate at this point was 980°C.

In comparison, diamond deposition was conducted using the apparatus mentioned above, under the indentical conditions except the cooling process; the substrate was not cooled by the water circulated by the circulator. The result after one hour was film diamond with thinkness of about 0.3μm. The temperature of the substrate, at this point, was 1400°C.

Example 2

Diamond was synthesized using chemical vapor deposition apparatus of this invention shown in Figure 2. The apparatus of this invention here has a reactor(1) with gas pipes(2 and 2') and a substrate holder(4) which rotates. Inside the reactor a thermionic emitter of tungsten(3) and several substrate of super hard alloy(5) were placed, with the substrate(5) being placed on the spherical substrate holder(4), which can be rotated to move the substrate to outside an irradiation range of the thermionic emitter(3). The cooling pipe(6') were installed outside an irradiation range of the thermionic emitter and the water was circulated inside the pipe(6') by the circulator(6).

First, the inside of the reactor(1) was evacuated through an

exhaust pipe(7). Then, 99 volume percent helium and 1 volume percent methane were introduced separately through gas pipes(2 and 2'). Diamond deposition was conducted with the thermionic emitter temperature at 2500°C, the distance between the substrate(5) and the thermionic emitter(3) 3mm, while applying 150 volts DC, making the substrate(5) positive, and the thermionic emitter(3) negative. Meanwhile, the substrate was cooled by both moving the substrate by the rotation of the holder(4) from within to outside the radiation range of the thermionic emitter(3), and by the substrate holder cooling structure consisting of a pipe(6'), which had been installed outside an irradiation range of the thermionic emitter, and a circulator(6). The result after one hour was high crystalline granular diamond 6.5μm thick. The substrate temperature at this point was 950°C.

In comparison, diamond deposition was conducted using the apparatus mentioned above under the indentical conditions except the cooling process; the substrate was not cooled by the circulated water, nor by the rotation of the holder. The result after one hour was diamond like carbon 0.7μm thick on the surface of the substrate. The substrate temperature at this point was 1370°C.

Example 3

Diamond deposition was conducted using the apparatus used in Example 2 under the following conditions: tungsten thermionic emitter temperature: 2000°C; substrate : super hard alloy with JIS (Japanese Industrial Standard) 10 equivalent; distance between the substrate and the thermionic emitter: 3mm; gas concentration: 95 volume percent helium and 5 volume percent methane. The substrate was cooled by the rotation of the substrate holder. The result after one hour was high crystalline film diamond 5μm thick on the substrate surface.

In comparison, diamond deposition was conducted under the identical conditions to the above deposition except the rotation of the substrate holder. The result after one hour was film diamond 0.5μm thick on the substrate surface. This film did not show diamond peak but graphite peak in Raman spectroscopic analysis.

Advantages

As seen in the above results, diamond chemical vapor deposition of this invention can produce diamond about ten times faster than the presently used methods, and the diamond produced by this apparatus is highly crystalline, granular diamond of better quality. In addition, the apparatus of this invention eliminates almost all the damage, is stable from the quality control point of view and can be applied to substrate of any material or any form.

Therefore, the diamond deposition apparatus of this invention is very useful in manufacturing parts for tools, nuclear reactor, electronics and precision machinery as well as material for parts used in various industrial fields.

4. Brief Explanation of the Figures

Figure 1 shows a symplified drawing of the diamond chemical vapor deposition apparatus of this invention used in Example 1. Figure 2 shows a symplfied drawing of the diamond chemical vapor deposition apparatus of this invention used in Example 2 and 3. In Figure 1 and 2, numerals denote the following: 1: reactor; 2 and 2': gas pipes; 3: thermionic emitter; 4: substrate holder; 5: substrate; 6: cooling water circulator; 6': cooling pipe and 7: exhaust pipe.

Applicant: Toshiba Tungaloy, Co., Ltd.

Figure 1

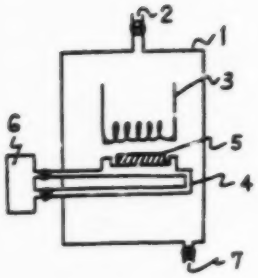

Figure 2